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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Blocked Polyisocyanates, Process for Their Preparation,
and Coating Materials and Coating Systems Produced
Therefrom

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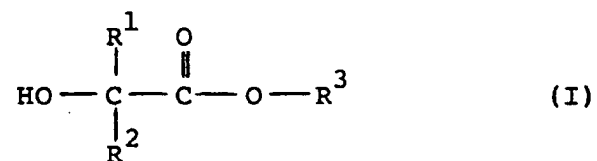
Notice: This application is as filed and may therefore contain an
incomplete specification.



ABSTRACT

Blocked Polyisocyanates, Process for Their
Preparation, and Coating Materials and
Coating Systems Produced Therefrom

Disclosed are blocked polyisocyanates having a free NCO content of less than 2% by weight in which the NCO groups are blocked with α -hydroxycarboxylic acid esters of the general formula:



(in which R^1 and R^2 are each hydrogen, alkyl, alkenyl, aralkyl or aryl group and R^3 is alkyl, alkenyl, aralkyl or aryl group). The blocked polyisocyanates are useful as adhesive or coating materials.

Blocked polyisocyanates, process for their preparation,
and coating materials and coating systems produced
therefrom

5 The present invention relates to blocked isocyanates, to
a process for their preparation and to their use in
adhesives and coating materials, especially in one-pack
PU stoving enamels and other coating systems.

10 The blocking of polyisocyanates for the temporary
protection of the NCO groups is a well-established
working method and is described, for example, in Houben-
Weyl, Methoden der Organischen Chemie [Methods of organic
chemistry] XIV/2, pp. 61-70. Curable compositions
15 comprising blocked polyisocyanates are used, for example,
in polyurethane coating materials. The coating films are
cured by reacting the thermally reactivated
polyisocyanates with polyols. A compilation of blocking
agents which are suitable in principle can be found, for
example, in Zeno W. Wicks Jr., Progress in Organic
Coatings 3 (1975) 73-79, 9 (1981) 3-28.

20 In coating applications, in order to cure within a time
of from 20 to 30 minutes, a large number of such blocking
agents require temperatures of more than 160°C. From an
economic standpoint, they therefore have excessively high
unblocking temperatures.

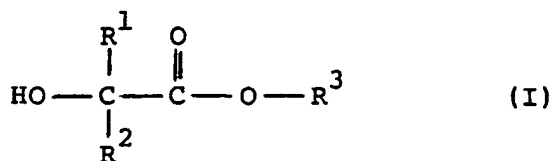
25 In the recent past, a small number of new systems have
been discovered which have low stoving temperatures of
around 100 to 140°C and stoving times of from 20 to 30
minutes. Thus oxime-blocked polyisocyanates are
described, for example, in DE-A 22 00 342, EP-A-0 432 257
30 and US-A-3,857,818. US-A-4,452,681, 4,452,930 and
4,452,963 describe urethane group-containing compounds,
prepared from polyisocyanates and α -hydroxy acid amides,
which are employed as low-temperature crosslinking agents
for both solvent-based and, in particular, water-based

compositions, such as electrodeposition coating materials. Both US-A-4,976,837 and EP-A-0 500 495 claim pyrazoles for the production of stoving enamels. Owing to the elimination of amine-containing compounds, some of which remain in the coating, the oxime-blocked or α -hydroxy acid amide-blocked polyisocyanates have a tendency to undergo yellowing. In the production of stoving enamels, the properties of the pyrazole-blocked polyisocyanates in respect of reactivity and curing times are very highly dependent on the blocking agent/polysiocyanate system employed. Only in a few systems can advantages
10 be discerned.

Therefore according to the present invention, it is attempted to provide novel, cost-effective, blocked isocyanates which eliminate the blocking agents at relatively low temperatures but nevertheless remain stable at ambient temperatures. Such polyisocyanates, unblocking at around 120 to 130°C, are to be suitable, particularly in combination with appropriate polyol components, for the production of one-pack (or one-can) stoving (or baking) enamels which exhibit a low
20 yellowing tendency.

Surprisingly, it has been found that alcohols having adjacent ester functions for the blocking of polyisocyanates, alone or in conjunction with known blocking agents essentially fulfill the desired properties.

The present invention therefore provides blocked polyisocyanates having a free NCO content of less than 2% by mass in which NCO groups are blocked with α -hydroxycarboxylic acid esters of the general formula:



(in which R^1 and R^2 are each hydrogen or an alkyl, alkenyl, aralkyl or aryl group and R^3 is an alkyl, alkenyl, aralkyl or aryl group, wherein these groups may contain a further substituent including one containing a heteroatom).

These groups preferably have 10 or less carbon atoms.

Preferred α -hydroxycarboxylic esters are those in which R^1 is hydrogen, R^2 is hydrogen or a methyl group and R^3 is an alkyl radical having 1 to 10 carbon atoms, more preferably 1 to 4 carbon atoms. Very preferred are glycolic acid esters with an alkyl group having 1 to 4 carbon atoms.

These compounds according to the invention are distinguished by a free NCO content of less than 2.0% by weight. Preferably, these blocked polyisocyanates have a blocked NCO content from 5 to 25% by weight. Their consistency at ambient temperature is generally liquid or solid.

The blocked polyisocyanates according to the invention can be prepared by reacting polyisocyanates with blocking agents such that, for each 0.8 to 1.2 mol of blocking agent, 1 NCO equivalent of the polyisocyanate component is reacted optionally in the presence of from 0.01 to 2.0% by weight of a catalyst. At least 10% by weight of, preferably at least 50% by weight of, more preferably entirely the blocking agents are the α -hydroxycarboxylic acid esters of the formula (I).

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The polyisocyanates to be blocked may be any organic polyisocyanates which are suitable for the crosslinking of compounds containing active hydrogen, i.e. aliphatic

(including cycloaliphatic), aromatic and heterocyclic polyisocyanates having at least two isocyanate groups and mixtures thereof. Representative examples of the polyisocyanates are aliphatic isocyanates such as alkylene

5 isocyanates, for example ethylene diisocyanate, propylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, 3-methylpentamethylene 1,5-diisocyanate (MPDI), hexamethylene diisocyanate (HDI), trimethylhexamethylene 1,6-diisocyanate (TMDI), especially the 2,2,4

10 and the 2,4,4 isomer and technical-grade mixtures of the two isomers, decamethylene diisocyanate and dodecamethylene diisocyanate, and cycloalkylene isocyanate, for example 1,3-cyclopentyl diisocyanate, 1,2-cyclohexyl diisocyanate, 1,4-cyclohexyl diisocyanate, ω,ω' -diisocyanato-1,4-dimethylcyclohexane, ω,ω' -diisocyanato-1,3-

15 dimethylcyclohexane, 1-methyl-2,4-diisocyanatocyclohexane, 4,4'-methylenebis(cyclohexyl isocyanate) (H_{12} MDI), and 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (IPDI). Representative examples of

20 polyisocyanates are also aromatic isocyanates such as aryl isocyanates, for example m-phenylene diisocyanate, p-phenylene diisocyanate, 4,4'-biphenyl diisocyanate, 1,4-naphthalene diisocyanate and 1,5-naphthalene diisocyanate, and alkaryl isocyanates, for example diisocyanatodiphenylmethane (MDI), in particular the 4,4' isomer, but also technical-grade mixtures of various isomers, for example the 4,4' and 2,4' isomers, diisocyanatomethylbenzene (TDI), in particular the 2,4 and the 2,6 isomer and technical-grade mixtures of the two isomers, 4,4'-

25 toluidine diisocyanate, 1,3-bis(isocyanatomethyl)benzene (XDI), m-tetramethylxylylene diisocyanate (TMXDI) and polymethylenepolyphenyl isocyanate, ring-substituted aromatic isocyanates, for example dianisidine diisocyanate, 4,4'-diphenyl ether diisocyanate and

30 chlorobiphenyl diisocyanate. Other highly suitable polyisocyanates include those which are obtainable by reacting polyisocyanates with themselves via isocyanate groups such as uretdiones or carbodiimide compounds which are formed by reaction of two isocyanate groups, or such

as isocyanurates, which are formed by reaction of three isocyanate groups. The polyisocyanates may likewise contain biuret or allophanate groups. Other compounds well-suited to the invention are polyisocyanate
5 prepolymers which contain on average more than one isocyanate group per molecule. They are obtained by preliminary reaction of a molar excess of, for example, one of the abovementioned polyisocyanates with an organic material which contains at least two active hydrogen
10 atoms per molecule, for example in the form of hydroxyl groups as in polyalkylene polyols.

Representative examples of the blocking agents are methyl glycolate, ethyl glycolate, butyl glycolate, ethyl lactate and butyl lactate.

15 The blocked polyisocyanates according to the invention are prepared by reacting from 0.8 to 1.2 mol of the blocking agent with one NCO equivalent of the polyisocyanate. It is possible if desired to add from 0.01 to 2.0 % by wt., preferably from 0.05 to 1.0 % by
20 wt., of a catalyst. The catalysts employed are conventional urethanization catalysts. Examples of such catalysts are metals, metal salts or metal complexes, such as lead tetraacetate, dibutyltin dilaurate, zinc octoate or tertiary amines such as triethylamine or 1,4-
25 diazabicyclo[2.2.2]octane. The reaction can be carried out at room temperature or higher temperatures, for example at between 50 and 130°C.

Blocking may be carried out in bulk or in the presence of suitable solvents. The matter of whether to employ a
30 solvent-free procedure depends largely on the subsequent application of the blocked polyisocyanate. If it is used to produce heat-curable PU powders, it is produced by a solvent-free method. When the blocked polyisocyanates according to the invention are employed as curing compo-
35 nent in the production of solvent-containing one-pack PU stoving enamels, preparation in solution is appropriate.

Suitable inert solvents are aromatic hydrocarbons, esters or ketones and, as extenders or diluants, aliphatic hydrocarbons.

5 The blocking of the polyisocyanate with the blocking agent is generally carried out in such a way that the blocking agent is metered into the polyisocyanate, which is heated to about 25 to 60°C and contains from 0.05 to 1.0 % by wt. of dibutyltin dilaurate as catalyst, based on the sum of polyisocyanate and blocking agent, in about 10 20 to 40 % by wt. of inert solvent at a rate such that the temperature of the reaction mixture does not exceed 100°C. When the addition of the blocking agent is at an end, the mixture is maintained at reaction temperature until almost complete reaction has taken place. In 15 general, one NCO equivalent of the isocyanate component reacts with one mol of blocking agent.

In the context of the invention it is also possible to replace some of the α -hydroxycarboxylic esters employed in accordance with the invention by known blocking 20 agents. Accordingly, the blocked polyisocyanates may contain at least 10 % by wt., preferably at least 50 % by wt., of radicals of α -hydroxycarboxylic esters and other blocking agents, for example oximes or secondary amines, provided the combination meets the demands which 25 are made of the blocked polyisocyanates.

The present invention also relates to adhesives, coating materials and coating systems which comprise the blocked polyisocyanates claimed. The blocked isocyanates according to the invention are combined with the customary 30 resins for PU coatings, i.e. preferably with hydroxyl-containing resins.

These compounds according to the invention are distinguished in that, in combination with an appropriate polyol and in the presence of suitable catalysts, they 35 cure within baking times of from 15 to 30 minutes at

temperatures of from 120 to 140°C.

Examples of suitable polyols are alkyd resins, polyester polyols, hydroxyl-containing polyacrylates, hydroxyl-containing polyurethane polymers, hydroxyl-containing polyurea polymers, hydroxyl-containing polyether polymers, hydroxyl-containing epoxy polymers and hydroxyl-containing polyepoxide/amine adducts. The epoxy polymers may be free from epoxide groups or may contain epoxide groups.

- 10 The molecular weights of the polyols may vary over a wide range, depending on the nature of the polyols and on the desired property profiles of the coating materials formed by reaction with the blocked polyisocyanates according to the invention. Polyester polymers, epoxy polymers and
- 15 alkyd polymers may have molecular weights in the range from 500 to 50,000, preferably between 1000 and 5000. Acrylate polymers may possess molecular weights of 100,000 or more. They are usually in the range from 3000 to 50,000.
- 20 The hydroxyl content of the polymeric polyols should be sufficient for the composition of polyol and blocked polyisocyanates to cure to give coating films having the appropriate service properties. The hydroxyl number of the polymeric polyol is usually at least 30 mg of KOH/g,
- 25 preferably between 70 and 300 mg of KOH/g.

The blocked polyisocyanates according to the invention constitute valuable crosslinking resins for suitable polyols in the production of stoving enamels, especially in one-pack PU stoving enamels.

- 30 The formulation of adhesives, coating materials and other coating systems from the blocked polyisocyanates and polyols is known in the art and therefore requires no further description here. The blocked polyisocyanate may

be separate to or an integral component with the compound containing active hydrogen. Thus, for example, a polyisocyanate may be blocked and present as a separate component together with the polyol. Alternatively, the polyisocyanate may also be partially blocked and may react with a polyol to give an ungelled compound. In the latter case, the resulting urethane forms an integral component with the polyol. The blocked polyisocyanate is present in both systems in a quantity which is sufficient to impart excellent curing properties to the curable composition. The ratio of equivalents of the NCO groups of the polyisocyanate to the polyol is typically in the range from 0.1:1 to 2:1, preferably from 0.8:1 to 1.2:1.

Of very great importance, finally, is the use of catalysts in the production of high-grade adhesives, coating materials and coating systems. Commonly, in the combination of blocked polyisocyanates with resins, catalysts are used to enable effective curing at relatively low temperatures. For example, metal salts and/or metal complexes are employed in quantities of from about 0.1 to 2.0 % by wt., in particular from 0.5 to 1.5 % by wt., based on the weight of the curable composition. The curing catalyst may be mixed with the other starting materials simultaneously in order to produce the composition, or may be added to the composition in any usual sequence.

The heat-curable compositions which are produced using the blocked polyisocyanates according to the invention may additionally comprise compounds containing active hydrogen and, if desired, fillers, pigments and other additives which are customarily used to produce heat-curable coatings.

The use of the coating composition in accordance with this invention ensures curing of the coating material at temperatures of from 120 to 240°C, preferably within a temperature range between 120 and 150°C. In this way,

high-quality coatings or finishes having low yellowing values are obtained. When the coating compositions were cured under the conditions given above, it was found that the systems had a greater than expected mass after stoving. The examples which follow illustrate the invention in more detail.

Example

A. Preparation of the α -hydroxycarboxylic esters used in accordance with the invention as blocking agents

Glycolic acid is dissolved in the respective alcohol and added to an initial suspension charge of methyl isobutyl ketone and p-toluenesulphonic acid. The reaction mixture is heated at reflux for 3-8 h. The mixture is cooled to room temperature and insoluble constituents are removed by filtration. Subsequent distillation of the filtrate yields the α -hydroxycarboxylic ester. Table 1 gives an overview of the composition and preparation of the α -hydroxycarboxylic esters.

20 Table 1:

| α -hydroxycarboxylic ester | Starting materials | | | |
|-----------------------------------|----------------------------------|-----------------------|----------|-----------------------|
| | α -hydroxycarboxylic acid | quantity employed [g] | alcohol | quantity employed [g] |
| methyl glycolate | glycolic acid | 76.05 | methanol | 96.12 |
| ethyl glycolate | glycolic acid | 76.05 | ethanol | 116.72 |

B. Examples 1 to 4 according to the inventionPreparation of polyisocyanates blocked with α -hydroxycarboxylic esters

0.01 to 5 % by wt. of dibutyltin dilaurate are added to one NCO equivalent of the polyisocyanate solution prepared at from 40 to 80°C in an inert solvent. Subsequently, with stirring, from 0.8 to 1.2 mol of the α -hydroxycarboxylic ester are added in portions at a rate such that the reaction temperature does not exceed 100°C. When the addition of the α -hydroxycarboxylic ester is at an end, heating is continued for a further 0.5 to 2 hours at from 50 to 100°C in order to complete the reaction.

Table 2 shows the composition and the chemical and physical data of the blocked isocyanates.

Table 2:

| Example No. | Blocked Polyisocyanates | | | | |
|-------------|-------------------------|-----------------------------------|-----------------------------|--------------------------------|--------------------|
| | isocyanate | α -hydroxycarboxylic ester | Free NCO content [I by wt.] | Blocked NCO content [I by wt.] | Melting range [°C] |
| 1 | isocyanate 1 | methyl glycolate | < 0.1 | 12.4 | 96 - 102 |
| 2 | isocyanate 2 | ethyl glycolate | < 0.1 | 13.4 | - |
| 3 | isocyanate 1 | butyl glycolate | < 0.1 | 11.2 | 63 - 65 |
| 4 | isocyanate 3 | butyl glycolate | < 0.1 | 12.6 | - |

Isocyanate 1 = 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane

Isocyanate 2 = 3-methylpentamethylene 1,5-diisocyanate

Isocyanate 3 = hexamethylene 1,6-diisocyanate

C. Examples I to VI according to the invention

Preparation of the polyurethane coating materials according to the invention

5 The blocked isocyanates listed in Table 2, in a stoichiometric ratio with polyols in accordance with the formulations described below, are pigmented in a conventional manner with rutile TiO_2 corresponding to a p.v.c. of 19 and formulated with appropriate additives.

10 The polyols are for example

- polyesters having a hydroxyl content of 1-5 % by weight
- polyacrylates having a hydroxyl content of 1-5 % by weight

15 In Table 3, Examples I to VI according to the invention are coating compositions. The formulated viscosity is about 60 sec, measured in a DIN 4 cup at 20°C. All numerical values relate to percentages by weight.

Table 3:

| | Components | Examples | | | | | |
|----|---------------------------|----------|------|------|------|------|------|
| | | I | II | III | IV | V | VI |
| | Blocked polyisocyanate 1 | - | - | 25.0 | 24.2 | - | - |
| 5 | Blocked polyisocyanate 2 | - | - | - | - | 22.0 | - |
| | Blocked polyisocyanate 3 | 25.7 | 25.0 | - | - | - | - |
| 10 | Blocked polyisocyanate 4 | - | - | - | - | - | 24.7 |
| | PE 1 | 21.4 | - | 21.8 | - | - | - |
| | PE 2 | 7.6 | - | 7.7 | - | - | - |
| | Acry 1 | - | 33.5 | - | 33.9 | 19.0 | - |
| | Acry 2 | - | - | - | - | 16.2 | 36.5 |
| 15 | TiO ₂ , Rutile | 31.0 | 31.2 | 30.3 | 29.7 | 28.7 | 29.7 |
| | DBTL, 10 % in BA | 1.8 | 1.8 | - | - | - | - |
| | DBTA, 10 % in BA | - | - | 5.2 | 5.2 | 5.1 | 5.1 |
| | Isophorone | 3.0 | 3.0 | 3.0 | 2.0 | 3.0 | 1.5 |
| 20 | 3-methoxy-n-butyl acetate | 5.0 | 5.0 | 5.0 | 4.0 | 5.0 | 2.0 |
| | MOPA | 2.0 | - | 1.0 | - | - | - |
| | SOLVESSO 100 | 2.0 | - | - | - | - | - |
| | FC 430, 10 % | 0.5 | 0.5 | - | - | - | 0.5 |
| | Byk 331, 10 % | - | - | 1.0 | 1.0 | 1.0 | - |

- 25 PE 1 - Oxyester^{*} EP-2 1439, OHN: 130 mg of KOH/g; Huls AG
 PE 2 - Oxyester^{*} Z 1261, OHN: 120 mg of KOH/g; Huls AG
 Acry 1 - Setalux^{*} C 1187, OHN: 118 mg of KOH/g; Akzo Chemicals

^{*} Trade-mark

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- Acry 2 - Setalux^{**} C 1151, OHN: 145 mg of KOH/g; Akzo Chemicals
 DBTA - Dibutyltin diacetate catalyst, Acima AG
 DBTL - Dibutyltin dilaurate catalyst, Ciba Geigy AG
 MOPA - 1-methoxy-2-propyl acetate, BASF AG
 5 FC 430 - Levelling agent, 3M Deutschland GmbH
 Byk 331^{**} - Levelling agent, Byk-Chemie GmbH

The formulated coating materials in the wet state are applied using a doctor blade to 1 mm steel panels and are cured under various curing conditions in a coating convection oven (CCO).

Tables 4 and 5 below are compilations of important processing data and coatings-relevant parameters.

Table 4:

| Example No. | Temperature of circulating air in the CCO [°C] | | | | | | |
|-------------|------------------------------------------------|-----|------|------|------|------|------|
| | 220 | 200 | 180 | 160 | 140 | 130 | 120 |
| | Residence time in the CCO [min] | | | | | | |
| I | 2.5 | 3.5 | 6.0 | 12.0 | 30.0 | * | * |
| II | 4.0 | 8.0 | 30.0 | * | * | * | * |
| III | * | * | 4.0 | 5.0 | 15.0 | 30.0 | 45.0 |
| IV | * | * | 3.0 | 4.0 | 8.0 | 20.0 | 45.0 |
| V | * | * | * | 7.0 | 20.0 | 45.0 | * |
| VI | 2.5 | 2.5 | 3.5 | 6.0 | 15.0 | 30.0 | * |

*) not tested

The physical properties of the coating films, as listed in Table 5, are representative - within the range of natural variation - for all of the curing conditions indicated in Table 4.

^{**}) Trade-mark

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Table 5:

| Example | LT (μm) | CH | HB | HK (°) | EI (mm) | BI | GG | |
|---------|-------------------------|----|-----|-----------|------------|----|-----|-----|
| | | | | | | | 20° | 60° |
| I | 25 - 35 μm | 0 | 125 | 180 | 9 | 60 | 76 | 94 |
| II | 25 - 35 μm | 0 | 125 | 160 | 6 | 50 | 52 | 85 |
| III | 25 - 35 μm | 0 | 118 | 182 | 9 | 60 | 71 | 92 |
| IV | 25 - 35 μm | 0 | 125 | 163 | 9 | 30 | 76 | 91 |
| V | 25 - 35 μm | 0 | 125 | 161 | 8 | 30 | 55 | 90 |
| VI | 25 - 35 μm | 0 | 143 | 168 | 8 | 30 | 49 | 90 |

LT = Layer thickness

10 HB = Buchholz indentation hardness, as per DIN 53 153

CH = Crosshatch, as per DIN 53 151

HK = König hardness, as per DIN 53 157

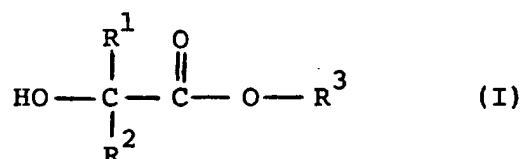
EI = Erichsen indentation, as per DIN 53 156

BI = Ball impact, as per ASTM D-2794/84

15 GG = Gardner gloss, as per ASTM D-523

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A blocked polyisocyanate having a free NCO content of less than 2% by weight in which NCO groups are blocked with a blocking agent, at least 10% by weight of the blocking agent being an α -hydroxycarboxylic acid ester of the general formula:



(in which R^1 and R^2 are each hydrogen or an alkyl, alkenyl, aralkyl or aryl group and R^3 is an alkyl, alkenyl, aralkyl or aryl group, wherein these groups may have a substituent which may contain a heteroatom).

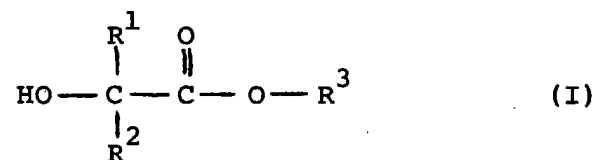
2. A blocked polyisocyanate according to claim 1, wherein R^1 and R^2 are each hydrogen or an alkyl, alkenyl, aralkyl or aryl group and R^3 is an alkyl, alkenyl, aralkyl or aryl group, where the groups have 10 or less carbon atoms.
3. A blocked polyisocyanate according to claim 1, wherein R^1 is hydrogen, R^2 is hydrogen or a methyl group and R^3 is an alkyl radical having 1 to 10 carbon atoms.
4. A blocked polyisocyanate according to claim 1, wherein the α -hydroxycarboxylic acid ester is a C_{1-4} alkyl ester of glycolic acid.

5. A blocked polyisocyanate according to claim 1, wherein the α -hydroxycarboxylic acid ester of the formula (I) is methyl glycolate, ethyl glycolate, butyl glycolate, ethyl lactate or butyl lactate.
6. A blocked polyisocyanate according to any one of claims 1 through 5, wherein at least 50% by weight of the blocking agent is the α -hydroxycarboxylic acid ester of the formula (I) and the remaining blocking agent is a member selected from the group consisting of oximes and secondary amines.
7. A blocked polyisocyanate according to any one of claims 1 through 5, wherein the blocking agent is solely the α -hydroxycarboxylic acid ester of the formula (I).
8. A blocked polyisocyanate according to any one of claims 1 through 7, wherein the polyisocyanate is an aliphatic, cycloaliphatic, aromatic or heterocyclic polyisocyanate.
9. A blocked polyisocyanate according to claim 8, wherein the polyisocyanate is
- 3,5,5-trimethyl-1-isocyanato-3-isocyanatomethylcyclohexane (IPDI),
- hexamethylene diisocyanate (HDI),
- 3-methylpentamethylene 1,5-diisocyanate (MPDI),
- trimethylhexamethylene 1,6-diisocyanate (TMDI),
- 4,4'-methylenebis(cyclohexyl isocyanato) (H_{12} MDI),
- diisocyanatodiphenylmethane (MDI),
- diisocyanatomethylbenzene (TDI),

1,3-bis(isocyanatomethyl)benzene (XDI) or
m-tetramethylxylylene diisocyanate (TMXDI).

10. A blocked polyisocyanate according to any one of claims 1 through 7, wherein the polyisocyanate contains a uretdione, isocyanurate, biuret or allophanate structures.

11. A process for the preparation of a blocked polyisocyanate which comprises reacting a polyisocyanate with a blocking agent such that, for each 0.8 to 1.2 mol of the blocking agent, 1 NCO equivalent of the polyisocyanate component is reacted in the presence of from 0.01 to 2.0% by weight of a catalyst, wherein at least 10% by weight of the blocking agent is an α -hydroxycarboxylic acid ester of the general formula:



(in which R^1 and R^2 are each hydrogen or an alkyl, alkenyl, aralkyl or aryl group and R^3 is an alkyl, alkenyl, aralkyl or aryl group, wherein these groups may contain a substituent which may contain a heteroatom).

12. A process according to claim 11, wherein R^1 is hydrogen, R^2 is hydrogen or a methyl group and R^3 is an alkyl radical having 1 to 10 carbon atoms.

13. A coating material consisting essentially of at least one active hydrogen-containing compound and a blocked polyisocyanate of any one of claims 1 through 10.

14. A coating material according to claim 13, which further contains a catalyst in an amount of from 0.1 to 2.0% by weight based on the total weight of the active hydrogen-containing compound and the blocked polyisocyanate.

15. A coating material according to claim 13, wherein the active hydrogen-containing compound is a polyol selected from the group consisting of alkyd resin, polyester polyol, hydroxyl-containing polyacrylate, hydroxyl-containing polyurethane polymer, hydroxyl-containing polyurea polymer, hydroxyl-containing polyether polymer, hydroxyl-containing epoxy polymer and hydroxyl-containing polyepoxide/amine adduct and is contained in such an amount that an NCO/OH equivalent ratio is 0.1:1 to 2:1.

16. A one-pack polyurethane stoving enamel based on an active hydrogen-containing compound and a blocked polyisocyanate of any one of claims 1 through 10.

17. An adhesive comprising a blocked polyisocyanate of any one of claims 1 through 10.

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